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ELECTROANALYTICAL INVESTIGATIONS. IV. USE OF ORTHOGONAL COLLOCA--ETC(11)

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Contract N00014-82-G-0017
Task No. NR 359-718
TECHNICAL REPORT NO. 11

Electroanalytical Investigations. IV. Use of Orthogonal Collocation for the Simulation of Quasireversible Electrode Processes under Potential Scan Conditions.

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Prepared for Publication in
Electrochimica Acta

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August 18, 1982

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| REPORT DOCUMENTATION PAGE | | 1. AD INSTRUCTIONS SEE FORM 1010-1, LINE 6, COLUMN 2. RECIPIENT'S CATALOG NUMBER |
|--|---|--|
| 1. REPORT NUMBER 11 | 2. GOVT ACCESSION NO. AD A118711 | 3. TYPE OF REPORT & PERIOD COVERED Technical Report # 11 |
| 4. TITLE (and Subtitle) Use of Orthogonal Collocation for the Simulation of Quasireversible Processes. | 5. AUTHOR(s) Bernd Speiser, Stanley Pons, and Anton Rieker | 6. PERFORMING ORG. REPORT NUMBER N00014-82-G-0017 |
| 7. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Alberta Edmonton, Alberta, Canada T6G 2G2 | 8. CONTRACT OR GRANT NUMBER(s) N00014-82-G-0017 | 9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. NR 359-718 |
| 10. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217 | 11. REPORT DATE August 18, 1982 | 12. NUMBER OF PAGES 29 |
| 13. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | 14. SECURITY CLASS. (of this report) Unclassified | 15. DECLASSIFICATION/DOWNGRADING SCHEDULE |
| 16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution unlimited. | | |
| 17. DISTRIBUTION STATEMENT (for the abstract entered in Block 20, if different from Report) Unlimited | | |
| 18. SUPPLEMENTARY NOTES | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by Block number) Electrochemistry, Orthogonal Collocation, Electron Transfer, Simulation, Cyclic Voltammetry | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by Block number) The procedure for simulating quasireversible electron transfer systems for cyclic voltammetry experiments is presented, and the procedure applied to several systems. The technique is based on orthogonal collocation. | | |

DD FORM 1473 EDITION OF 1 NOV 55 IS OBSOLETE
1 JAN 73 S/N 010-11 010-6081

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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ELECTROANALYTICAL INVESTIGATIONS. IV.
USE OF ORTHOGONAL COLLOCATION FOR THE SIMULATION OF
QUASIREVERSIBLE ELECTRODE PROCESSES UNDER
POTENTIAL SCAN CONDITIONS

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ABSTRACT

The method of orthogonal collocation is used to discretize the differential equations describing quasireversible electrode processes under conditions of potential scanning. The resulting set of ordinary differential equations is solved to give numerical simulations. The numerical values are compared to literature data. A method for optimization of the dimensionless parameter α is given.

INTRODUCTION

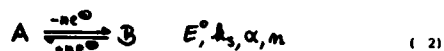
The mathematical description of electrochemical processes at stationary electrodes yields partial differential equations of the type

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - f(c) \quad (1)$$

for each species, where $f(c)$ is determined by the homogeneous kinetics of the electrochemically produced intermediates and the substrate and x is a distance coordinate. The initial condition normally is that the substrate is the only species present in solution and is homogeneously distributed in the x direction.

The boundary conditions are dictated by the experiment performed and by the kind of electron transfer, i.e. reversible or irreversible. It has been shown for a variety of boundary conditions [1-4] that orthogonal collocation [5,6] provides a powerful, fast, and easily applied method to simulate kinetic diffusion problems of this kind. Up to now, however, only boundary conditions related to reversible electron transfer reactions have been used.

We now report the theory for application of this mathematical method to quasireversible electrode mechanisms:



where the electrode reaction of A to B is described by a standard potential E^0 , a standard rate constant for electron transfer k_s , the transfer coefficient α and the number n of transferred electrons. Product B may react in a chemical reaction (3) with a homogeneous rate constant k .

INITIAL AND BOUNDARY CONDITIONS

To simulate a reaction scheme (2)-(3) we have to solve equations of the type (1) for three species A, B and C (assuming equal diffusion coefficients for each species):

$$\frac{\partial c_A}{\partial t} = D \frac{\partial^2 c_A}{\partial x^2} \quad (4)$$

$$\frac{\partial c_B}{\partial t} = D \frac{\partial^2 c_B}{\partial x^2} - k c_B \quad (5)$$

and

$$\frac{\partial c_C}{\partial t} = D \frac{\partial^2 c_C}{\partial x^2} + k c_B \quad (6)$$

The calculation of C_C is not essential to simulate purely electrochemical responses for this reaction scheme. However, if one wishes to do so, this calculation may be included without any problem.

The initial conditions are:

$t=0, 0 \leq x \leq \infty$:

$$c_A = c_A^0 \quad (7)$$



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$$C_B = C_C = 0$$

(8)

The boundary conditions at an infinite distance from the electrode are given by
 $t > 0, x \rightarrow \infty$:

$$C_A \rightarrow C_A^*$$

(9)

$$C_B = C_C \rightarrow 0$$

(10)

whereas at the electrode
 $t > 0, x = 0$:

$$\left(\frac{\partial C_A}{\partial x} \right)_{x=0} = - \left(\frac{\partial C_B}{\partial x} \right)_{x=0} \quad (11)$$

$$D \left(\frac{\partial C_A}{\partial x} \right)_{x=0} = k_f C_A(0,t) - k_b C_B(0,t) \quad (12)$$

holds. Here (7.6)

$$k_f = k_s \cdot \exp[(1-\alpha)nF/RT (E-E^0)] \quad (13)$$

and

$$k_b = k_s \cdot \exp[-\alpha nF/RT (E-E^0)] \quad (14)$$

Introducing Nicholson's definitions [8,9] for potential scan conditions (cyclic voltammetry)

$$\Theta = \exp[nF/RT (E^0 - E_{start})] \quad (15)$$

$$S_A(t) = \begin{cases} e^{-\alpha t} & t < t_\lambda \\ e^{\alpha t - 2\alpha t_\lambda} & t_\lambda < t < 2t_\lambda \end{cases} \quad (16a)$$

(16b)

and

$$\alpha = \frac{nF}{RT} V \quad (17)$$

(where E_{start} is the starting potential of the potential sweep with sweep speed v and t_λ is the time when the sweep is reversed), equation (12) can be changed to

$$D \left(\frac{\partial C_A}{\partial x} \right)_{x=0} = k_s S_A(t)^{-(1-\alpha)} \Theta^{1-\alpha} [C_A(0,t) - C_B(0,t) S_A(t) \Theta] \quad (18)$$

Because species C is not electroactive, its flux at $x = 0$ is always zero:

$$t > 0, x = 0: \left(\frac{\partial C_C}{\partial x} \right)_{x=0} = 0 \quad (19)$$

The system of partial differential equations (4)-(6) has to be solved under the initial conditions (7) and (8) and the boundary conditions (9)-(11), (18) and (19).

TRANSFORMATION INTO A DIMENSIONLESS SYSTEM OF EQUATIONS

We have to transform this system of partial differential equations and the conditions under which it is to solve into a

dimensionless form. We use the following transformation equations:

$$T' = \alpha t \quad (20)$$

$$X = x/L \quad (21)$$

$$C_A' = C_A/C_A^0 \quad (22)$$

$$C_B' = C_B/C_A^0 \quad (23)$$

$$C_C' = C_C/C_A^0 \quad (24)$$

$$\chi = A/a \quad (25)$$

$$Y = A_2/\sqrt{aD} \quad (26)$$

and

$$\beta = D/aL^2 \quad (27)$$

where L is a distance from the electrode where no diffusion occurs during the simulation. Thus, the dimensionless system is

$$\frac{\partial C_A'}{\partial T'} = \beta \frac{\partial^2 C_A'}{\partial X^2} \quad (28)$$

$$\frac{\partial C_B'}{\partial T'} = \beta \frac{\partial^2 C_B'}{\partial X^2} - \chi C_B' \quad (29)$$

$$\frac{\partial C_C'}{\partial T'} = \beta \frac{\partial^2 C_C'}{\partial X^2} + \chi C_B' \quad (30)$$

under the conditions

$$T' = 0, 0 \leq X \leq 1:$$

$$C_A' = 1 \quad (31)$$

$$C_B' = C_C' = 0 \quad (32)$$

$$T' > 0, X = 1:$$

$$C_A' = 1 \quad (33)$$

$$C_B' = C_C' = 0 \quad (34)$$

$$T' > 0, X = 0: \left(\frac{\partial C_A'}{\partial X} \right)_{X=0} = - \left(\frac{\partial C_B'}{\partial X} \right)_{X=0} \quad (35a)$$

$$\left(\frac{\partial C_C'}{\partial X} \right)_{X=0} = 0 \quad (35b)$$

$$\left(\frac{\partial C_C'}{\partial X} \right)_{X=0} = \frac{1}{\sqrt{\beta}} S_A(T')^{-1/2} \Theta^{-1/2} [C_A'(0,T') - C_B'(0,T') S_A(T') \Theta] \quad (36)$$

with

$$S_A(T') = \begin{cases} \exp(-T') & T' < T_A' \\ \exp(T' - 2T_A') & T_A' < T' < 2T_A' \end{cases} \quad (37a)$$

$$(37b)$$

DISCRETISATION WITH ORTHOGONAL COLLOCATION

Now we use orthogonal collocation to derive a system of simultaneous ordinary differential equations from each of the three partial differential equations (28)-(30). We fit the coefficients of a polynomial in $C^0(x,t)$ such that the differential equations are fulfilled exactly at certain points. It has been shown that a very efficient collocation method can be constructed if we use orthogonal polynomials and if those points are the zeroes of the polynomial [6]. Furthermore, in this case, the distance derivatives of the concentration at these "collocation points" are given by [1,5,6]

$$\frac{dC^0}{dX} \Big|_{x_i} = \sum_{j=1}^{N+2} A_{i,j} C^0(x_j, T') \quad (38)$$

$$\frac{d^2 c^0}{dx^2} \Big|_{x_i} = \sum_{j=2}^{N+2} B_{ij} c^0(x_j, T') \quad (39)$$

where the $A_{1,j}$ and $B_{1,j}$ are matrix elements only dependent on the kind and degree of the polynomial chosen. A polynomial of degree N has N roots in the open interval between zero and one and we have to include the boundary points at $x = 0$ and $x = 1$. Thus, the dummy variable j varies from 1 to $N+2$.

Substituting the second derivatives with respect to x in equation (28) we get

$$\frac{dc_A^0}{dT'} \Big|_{x_i} = \beta \sum_{j=2}^{N+2} B_{ij} c_A^0(x_j, T') \quad (40)$$

where the sum can be expanded and the boundary conditions (13) be introduced:

$$\frac{dc_A^0}{dT'} \Big|_{x_i} = \beta \left\{ B_{i,1} c_A^0(0, T') + B_{i,N+2} c_A^0(1, T') + \sum_{j=2}^{N+2} B_{ij} c_A^0(x_j, T') \right\} \quad (41)$$

The concentration of species A at the electrode surface is not known explicitly but may be derived from the boundary conditions (35) and (36). Using (38), equation (35) yields:

$$\sum_{j=2}^{N+2} A_{1j} c_A^0(x_j, T') = - \sum_{j=2}^{N+2} A_{1j} c_B^0(x_j, T') \quad (42)$$

$$\text{or} \quad c_A^0(0, T') = -c_B^0(0, T') - \frac{A_{1,N+2}}{A_{1,1}} \left\{ A_{1,N+2} + \sum_{j=2}^{N+2} A_{1j} c_A^0(x_j, T') + \sum_{j=2}^{N+2} A_{1j} c_B^0(x_j, T') \right\} \quad (43)$$

Equation (36) gives (again using (38))

$$\sum_{j=2}^{N+2} A_{1j} c_A^0(x_j, T') = \frac{\gamma}{\sqrt{\pi}} S_A(T')^{-1/2} \theta^{-(N+2)} [c_A^0(0, T') - c_B^0(0, T') S_A(T') \theta] \quad (44)$$

or after expansion of the sum, collection of the terms containing $c_A^0(0, T')$ and solution for $c_A^0(0, T')$:

$$c_A^0(0, T') = \left[S_A(T')^{-1/2} \theta^{-N} - \frac{A_{1,1}}{\sqrt{\pi} S_A(T') \theta} \right] c_A^0(0, T') - \frac{A_{1,N+2} + \sum_{j=2}^{N+2} A_{1j} c_A^0(x_j, T')}{\sqrt{\pi} S_A(T') \theta} \quad (45)$$

Equations (43) and (45) can be solved for $c_A^0(0, T')$:

$$c_A^0(0, T') = \frac{\sqrt{\pi} S_A(T') \theta^{-N} - A_{1,1}}{A_{1,1} [A_{1,1} - \sqrt{\pi} S_A(T') \theta^{-N} - \sqrt{\pi} S_A(T') \theta^{-(N+2)}]} \times [A_{1,N+2} + \sum_{j=2}^{N+2} A_{1j} c_A^0(x_j, T') + \frac{\gamma}{\sqrt{\pi}} S_A(T') \theta^{-N} \sum_{j=2}^{N+2} A_{1j} c_B^0(x_j, T')] \quad (46)$$

Now it is possible to substitute for $c_A^0(0, T')$ in equation (41)

and we finally get

$$\frac{dc_A^0}{dT'} \Big|_{x_i} = \beta \left\{ - \frac{B_{i,1}}{A_{1,1} [A_{1,1} - \sqrt{\pi} S_A(T') \theta^{-N} - \sqrt{\pi} S_A(T') \theta^{-(N+2)}]} \times [A_{1,N+2} + \sum_{j=2}^{N+2} A_{1j} c_A^0(x_j, T') + \frac{\gamma}{\sqrt{\pi}} S_A(T') \theta^{-N} \sum_{j=2}^{N+2} A_{1j} c_B^0(x_j, T')] + B_{i,N+2} + \sum_{j=2}^{N+2} B_{ij} c_A^0(x_j, T') \right\} \quad (47)$$

It follows from equation (29) after insertion of (39), expansion of the sum and introduction of the boundary condition (34):

$$\frac{dc_B^0}{dt'} \bigg|_{x=0} = \beta \left\{ B_{1,1} c_B^0(0,T') + \sum_{j=2}^{N+1} B_{1,j} c_B^0(x_j,T') \right\} - K c_B^0(x_1,T') \quad (48)$$

Again, $c_B^0(0,T')$ may be calculated. If we insert (43) into (45) we arrive at

$$c_B^0(0,T') = - \frac{1}{A_{1,1} [A_{1,1} - \sqrt{\rho} S_1(T')^{-1/2} \theta^{-(1/2)} - \sqrt{\rho} S_1(T')^0 \theta^0]} \times \left\{ [A_{1,1} - \sqrt{\rho} S_1(T')^{-1/2} \theta^{-(1/2)}] \sum_{j=2}^{N+1} A_{1,j} c_B^0(x_j,T') - \sqrt{\rho} S_1(T')^{-1/2} \theta^{-(1/2)} [A_{1,N+1} + \sum_{j=2}^{N+1} A_{1,j} c_A^0(x_j,T')] \right\} \quad (49)$$

which may be substituted for $c_B^0(0,T')$ in equation (48), yielding the time derivative of the concentration of species B at the collocation points:

$$\frac{dc_B^0}{dt'} \bigg|_{x_i} = \beta \left\{ - \frac{B_{1,1}}{A_{1,1} [A_{1,1} - \sqrt{\rho} S_1(T')^{-1/2} \theta^{-(1/2)} - \sqrt{\rho} S_1(T')^0 \theta^0]} \times \left\{ [A_{1,1} - \sqrt{\rho} S_1(T')^{-1/2} \theta^{-(1/2)}] \sum_{j=2}^{N+1} A_{1,j} c_B^0(x_j,T') - \sqrt{\rho} S_1(T')^{-1/2} \theta^{-(1/2)} [A_{1,N+1} + \sum_{j=2}^{N+1} A_{1,j} c_A^0(x_j,T')] \right\} + \sum_{j=2}^{N+1} B_{1,j} c_B^0(x_j,T') \right\} - K c_B^0(x_1,T') \quad (50)$$

To express the corresponding derivative for species C we insert (39) into equation (38), expand and use the boundary condition (34):

$$\frac{dc_C^0}{dt'} \bigg|_{x_i} = \beta \left\{ B_{1,1} c_C^0(0,T') + \sum_{j=2}^{N+1} B_{1,j} c_C^0(x_j,T') \right\} + K c_B^0(x_1,T') \quad (51)$$

The concentration of species C at the electrode surface ($x = 0$) may be derived from equation (35b) as

$$c_C^0(0,T') = - \frac{1}{A_{1,1}} \sum_{j=2}^{N+1} A_{1,j} c_C^0(x_j,T') \quad (52)$$

and used to express the time dependence of c_C^0 finally:

$$\frac{dc_C^0}{dt'} \bigg|_{x_i} = \beta \left\{ - \frac{B_{1,1}}{A_{1,1}} \sum_{j=2}^{N+1} A_{1,j} c_C^0(x_j,T') + \sum_{j=2}^{N+1} B_{1,j} c_C^0(x_j,T') \right\} + K c_B^0(x_1,T') \quad (53)$$

Equations (47), (50) and (53) define a system of $3 \times N$ ordinary differential equations which may be solved by computer subroutines. We note the formal similarity of these expressions with the corresponding equations derived for an EC mechanism with a reversible electron transfer reaction [2] under cyclic voltammetric conditions. The equations derived here for quasireversible electron transfers may be used also for the simulation of more complicated electrode reactions with multistep homogeneous reactions or reactions of the ECE type by changing the kinetic term [i.e. $f(c)$ in equation (1)] to the appropriate expression. This makes the application of orthogonal collocation especially easy once the basic equations for a specific boundary value problem have been derived and is one advantage of this method.

CALCULATION OF THE CURRENT

The current through the working electrode is given by

$$i = nFA D \left(\frac{\partial c_A}{\partial x} \right)_{x=0} \quad (54)$$

We have shown [2], that Nicholson and Shain's current function $i(x,t)$ [9] can be related to the dimensionless quantities used in

the transformation equations (20)-(24) by

$$X(x,t) = \frac{i}{nFAc_A \sqrt{D\omega}} = \sqrt{\frac{D}{\pi}} \left(\frac{\partial c_A}{\partial x} \right)_{x=0} \quad (55)$$

Thus, calculation of i or $X(x,t)$ requires the calculation of the first derivative of c_A with respect to x at the electrode surface. This may be done from equation (36) using equations (46) and (49). It follows

$$X(x,t) = \sqrt{\frac{D}{\pi}} \left\{ - \frac{1}{[A_{N+1} \sqrt{D} S_N(T)^{-(N+1)} b^{-(N+1)} - \sqrt{D} S_N(T)^N \theta^N]} \right. \\ \left. \left[\sqrt{D} S_N(T)^{-(N+1)} b^{-(N+1)} [A_{N+2} + \sum_{j=2}^N A_{j+2} c_j^*(x_j, T)] \right. \right. \\ \left. \left. - \sqrt{D} S_N(T)^N \theta^N \sum_{j=2}^N A_{j+1} c_j^*(x_j, T) \right] \right\} \quad (56)$$

OPTIMIZATION OF THE DIMENSIONLESS PARAMETER β

In the case of a reversible electrode reaction it has been shown that the value of the dimensionless parameter β has a significant influence on the accuracy of the simulation [2]. Also, a method to optimize this value in terms of stability of the solution of the differential equation system has been given [10].

Starting with Milston's stability criterion [11] for Hamming's predictor-corrector-integration method

$$h < \frac{0.65}{|f_y|} \quad (57)$$

which relates the maximum stepwidth of the integration h to the absolute value of

$$f_y = \frac{\partial \left(\frac{\partial c}{\partial x} \right)}{\partial c} \quad (58)$$

for equations of type (28-30), it is possible to calculate a maximum value of β without causing instability of the solution. Inequality (57) must be fulfilled for all species and collocation points. From equation (47) follows

$$f_y = \beta \left\{ - \frac{\frac{\partial c_A}{\partial x}}{A_{N+1} [A_{N+1} \sqrt{D} S_N(T)^{-(N+1)} b^{-(N+1)} - \sqrt{D} S_N(T)^N \theta^N]} \right. \\ \left. (A_{N+1} \sqrt{D} S_N(T)^N \theta^N) A_{N+1} + B_{N+1} \right\} \quad i=2, \dots, N+1 \quad (59)$$

In analogy equation (50) yields

$$f_y = \beta \left\{ - \frac{\frac{\partial c_A}{\partial x}}{A_{N+1} [A_{N+1} \sqrt{D} S_N(T)^{-(N+1)} b^{-(N+1)} - \sqrt{D} S_N(T)^N \theta^N]} \right. \\ \left. (A_{N+1} \sqrt{D} S_N(T)^{-(N+1)} b^{-(N+1)}) A_{N+1} + B_{N+1} \right\} - X \quad i=2, \dots, N+1 \quad (60)$$

while equation (53) gives

$$f_y = \beta \left\{ - \frac{B_{N+1}}{A_{N+1}} A_{N+1} + B_{N+1} \right\} \quad (61)$$

As in the case of a reversible electron transfer, we have to make sure that (57) is fulfilled at the extreme points of a possible scan, i.e. $S_1(T') = 0$ ($T' = T_1' > 0$) and $S_1(T') = 1$ ($T' = 0$).

Inserting the corresponding expressions for f_y into inequality (57) would yield inequalities which are difficult to solve for β . If we assume, however, that the scan starts at a potential well before the standard potential (which is the general experimental procedure) we can set

$$\theta \gg 1$$

(62)

Thus, for $\alpha > 0$

$$\theta^{\alpha} \gg 1$$

(63a)

and

$$\theta^{-(1-\alpha)} \ll 1$$

(63b)

Equations (59) and (60) reduce for $S_1(T') = 0$ to

$$f_y = \beta \left\{ -\frac{B_{i,1}}{A_{i,1}} A_{i,1} + B_{i,1} \right\} \quad i=2, \dots, N+1 \quad (64)$$

and

$$f_y = \beta \left\{ -\frac{B_{i,1}}{A_{i,1}} A_{i,1} + B_{i,1} \right\} - \chi \quad i=2, \dots, N+1 \quad (65)$$

while for $S_1(T') = 1$

$$f_y = \beta \left\{ -\frac{B_{i,1}}{A_{i,1}} A_{i,1} + B_{i,1} \right\} \quad i=2, \dots, N+1 \quad (66)$$

and

$$f_y = \beta \left\{ -\frac{B_{i,1}}{A_{i,1} \sqrt{\rho} \theta^{\alpha}} A_{i,1} + B_{i,1} \right\} - \chi \quad i=2, \dots, N+1 \quad (67)$$

Finally stability is maintained if inequalities (68)-(70) are fulfilled

$$h < \begin{cases} \frac{0.65}{\left| \beta \left\{ -\frac{B_{i,1}}{A_{i,1}} A_{i,1} + B_{i,1} \right\} \right|} & i=2, \dots, N+1 & (68) \\ \frac{0.65}{\left| \beta \left\{ -\frac{B_{i,1}}{A_{i,1}} A_{i,1} + B_{i,1} \right\} - \chi \right|} & i=2, \dots, N+1 & (69) \\ \frac{0.65}{\left| \beta \left\{ -\frac{B_{i,1}}{A_{i,1} \sqrt{\rho} \theta^{\alpha}} A_{i,1} + B_{i,1} \right\} - \chi \right|} & i=2, \dots, N+1 & (70) \end{cases}$$

As pointed out for the reversible case [10], h has to be chosen as large as possible to give reliable results.

RESULTS OF THE CALCULATIONS

Calculations using the theory derived above have been performed on an Amdahl 470/V6 computer using a dialog program for data input*. Trial functions have been Legendre polynomials with different degree N . Table 1 shows the variation of peak potential separation with N compared to the "reference" value given by Nicholson [8]. The integration step width was 0.5 (mV), i.e. the simulated cyclic voltammogram between 0.0 and 0.3 (V) was constructed from 1200 data points. The cpu-time needed for different N is also given in Table 1.

For $N > 9$ the peak potential separation is essentially the same as given by Nicholson, the difference being 0.5 (mV), i.e. the same value as the integration step width. For smaller N ΔE_p

* Copies of the program which also contains other electrochemical reaction models are available on request.

deviates considerably. The cpu-time, however, decreases. According to this result, all further simulations have been performed with $N = 9$. Table 2 shows variation of ΔE_p with the kinetic parameter ψ' which is connected to Nicholson's parameter ψ [8] by

$$\psi' = \psi \sqrt{\pi} \quad (71)$$

The maximum deviation from Nicholson's data is 1.5 (mV), a very low value considering that ΔE , the integration step width, is 0.5 (mV). It should be noted here that Nicholson's values are simulated as well. With approximately 2.5 cpu-seconds needed for 1200 data points, the program works fast and efficient.

CONCLUSION

The technique of orthogonal collocation can be applied to simulate quasireversible electrode processes under potential sweep conditions. The equations describing the time dependence of the concentration of all species are formally very similar to those derived for reversible electron transfers. The dimensionless parameter δ can be optimised in terms of stability of the solution of the differential equation system. The numerical results calculated for the "pure" quasireversible electron transfer (i.e. without homogeneous kinetic complications) are very close to the reference values given by Nicholson [8] and computed by a totally different method.

The application of this work is obviously the interpretation

of more complicated electrode reaction mechanisms where homogeneous chemical reactions are coupled to the quasireversible electron transfer. The expansion of the theory given here to those cases is, as usual in orthogonal collocation calculations, easily done. Simulation and comparison to experiments with real substrates undergoing complicated reaction sequences will be shown in a further paper.

ACKNOWLEDGEMENTS

S.P. and B.S. gratefully acknowledge financial support from the Office of Naval Research and the Chemistry Department of the University of Alberta. In addition, B.S. and A.R. gratefully acknowledge the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg for financial support.

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Table 1. Simulations of a quasireversible electrode process with polynomials of different degree N .

| N | ΔE_p (mV) ^{a)} | x_p^{ox} | x_p^{red} | cpu-time (s) | ΔE_p (mV) ^{b)} |
|-----|---------------------------------|------------|-------------|--------------|---------------------------------|
| 6 | 110.5 | -0.4040 | 0.1989 | 1.923 | 105 |
| 7 | 103.0 | -0.4036 | 0.2272 | 2.044 | 105 |
| 8 | 104.0 | -0.4036 | 0.2357 | 2.169 | 105 |
| 9 | 104.5 | -0.4036 | 0.2369 | 2.473 | 105 |
| 10 | 104.5 | -0.4036 | 0.2370 | 2.536 | 105 |

a) This work, $\Delta E = 0.5$ (mV), $\gamma' = 0.88623$.

b) Nicholson, ref. [8], $\gamma = 0.5$ ($\gamma' = 0.88623$).

Table 2. Simulations of a quasireversible electrode processes by orthogonal collocation, variation of ϕ' .

| ϕ' ^{a)} | ϕ' ^{b)} | ΔE_p ^{a)} (mV) | ΔE_p ^{b)} (mV) |
|-----------------------|-----------------------|---------------------------------|---------------------------------|
| 0.17725 | 0.1 | 210.5 | 212 |
| 0.44111 | 0.25 | 140.0 | 141 |
| 0.62036 | 0.35 | 120.5 | 121 |
| 0.88623 | 0.5 | 104.5 | 105 |
| 1.3293 | 0.75 | 90.5 | 92 |
| 1.7725 | 1 | 83.0 | 84 |
| 3.5449 | 2 | 74.5 | 72 |
| 5.3174 | 3 | 67.0 | 68 |
| 7.0898 | 4 | 65.5 | 66 |
| 8.8623 | 5 | 64.0 | 65 |
| 10.6347 | 6 | 63.5 | 64 |
| 12.4072 | 7 | 62.5 | 63 |
| 35.4491 | 20 | 60.0 | 61 |

a) This work, $\Delta E = 0.5$ (mV), $N = 9$, $|E^* - E_1| = 0.14$ (V).

b) Nicholson, ref. [8], $|E^* - E_1| = 0.141$ (V).

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